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Biochar as a Substitute for Carbon Black in Lithographic Ink Production

by

Vanessa Hulse

A Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree of

Master of Science

in

Chemistry

School of Chemistry and Materials Science
College of Science
Rochester Institute of Technology
Rochester, NY
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School of Chemistry and Materials Science

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ABSTRACT

Replacing carbon black with biochar, a more sustainable carbon negative material, in commercial inks will be presented. The overall project goal was to produce an optimal feedstock for biochar through impurity removal techniques. Biochar is most commonly used in soil applications or water remediation, due to its highly porous nature, leading to high contaminant adsorption. This project however, focuses on biochar as a pigment for lithographic inks. When raw boxboard or recycled paper pulp was subjected to pyrolysis, an appreciable amount of mineral impurities remained. These harder mineral impurities result in poor black coverage power. Harder mineral impurities also made mill processing more inefficient. A reasonable and sustainable purification process was required. New feedstock processing techniques were developed to remove, SiO_2 , TiO_2 , and CaO . Treatment effectiveness was confirmed using x-ray analysis to determine carbon and inorganic contaminant changes. The most effective treatments were a phosphoric acid treatment, and a floatation treatment which increased the carbon percentage 3% and 4%, respectively. The least effective contamination removal methods were flotation, acid digestion and hydrogen peroxide treatments, which decreased the carbon percent by 0%, 3%, and 6%, respectively. A significant increase in carbon content, up to 98% carbon by weight, was achieved when using the optimized pre-treatment processes. The biochar was then subjected to a range of pyrolysis temperatures ranging from 550°C and 1600°C in order to obtain a maximum black ink covering power. Lithographic printing inks were then formulated and print tested. With new contamination processing techniques, more biochar feedstocks can be introduced to the industry. Introducing more feedstocks, such as non-recyclable boxboard waste, has the potential to increase the sustainability of this technology. There is additional sustainable potential if current Technical Association of the Pulp and Paper Industry (TAPPI) covering power and color standards are loosened for the sake of producing sustainable inks.

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List of Abbreviations:

EDS	Energy Dispersive X-Ray Spectroscopy
EDXRF	Energy Dispersive X-Ray Fluorescence Analyzer
FTIR	Fourier-Transform Infrared Spectroscopy
HTC	Hydrothermal Carbonization
LCA	Life Cycle Assessment
SEM	Scanning Electron Microscopy
TAPPI	Technical Association of the Pulp and Paper Industry

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CHAPTER 1 – INTRODUCTION

1.1. Topic Statement

This research was performed to replace carbon black with an alternative, sustainable pigment in lithographic printing inks. Biochar produced from renewable feedstocks was studied to match current black lithographic ink parameters. To create a comparable ink pigment, a cleaning process of the original feedstock was studied. In addition to the biochar pigment, coal was tested as an alternative printing ink pigment, to sequester the carbon in coal rather than releasing it back into the environment.

1.2. Significance of Topic

Biochar is a sustainable alternative to carbon black that is currently being used as a pigment in commercial inks. Biochar, a recycled material, will replace carbon black, a virgin material. Therefore, pigment replacement has the potential to save money and resources.

The main feedstock, non-recyclable boxboard waste, is of particular interest because it is a sustainable source from waste materials. Currently, this boxboard waste goes directly into a landfill when it can no longer be recycled. However, by using it as an ink pigment, it can be recycled another time, closing the production loop for both boxboard at the end of life, and ink pigment at the beginning of life. This research can not only be applied to other potential biochar pigments, but other biochar applications as well. The cleaning processes employed in this research can be another method of tuning biochar production, in addition to those already employed, including the alteration of production parameters.

Lastly, this research topic has economic importance. There is strong evidence that suggests petroleum products will increase in price until it is no longer beneficial to use and produce oil.^{1,2} Having a new material in place before the dramatic increase in price or the final depletion of oil reserves occurs can ultimately save money for the ink industry in the long run.

1.3. Reason for Interest in This Topic

I have a particular interest in producing a more sustainable black lithographic ink because it brings together two of my academic interests, chemistry and sustainability. This research project has allowed me to approach a sustainability issue from a chemistry perspective. It is a passion of mine to bring sustainability perspectives into innovation into the chemistry field. Since I am passionate about both, it has been my desire to move forward in my career in a way that can incorporate both. This research has allowed me to develop these two passions even further together.

CHAPTER 2 – Theoretical Basis

2.1. Lithographic Inks and Offset Printers

Lithography is a form of commercial printing that is used to produce printed books, newspapers, and packaging. All inks are composed of a pigment and a way to suspend that pigment and then put it on a new substrate. For lithographic inks there are specific names given to these components, more specifically they are called the pigment and the vehicle or the medium.³ The pigment is what gives the ink the specific color that is desired. The vehicle suspends the pigment and facilitates transfer to the substrate.

The relationship of these two to each other is also important. There must be enough pigment in the vehicle to be spread evenly throughout the ink. For lithographic inks especially the properties of the combination of these must result in an ink that has a strong color and have the correct spreading. Another important property that these inks must possess is that they must be resistant to acids as acids are generally used when printing with the ink.⁴ There are also certain substances that can be added to these inks to make these properties align more with the goals of the project.³ Such additives include dispersants, drying agents, and waxes. All additives can alter ink rheological properties to optimize the ink for individual applications. Lithographic inks are oil-based inks, which aids in the specific printing process used.

There are two main ways an image can be printed onto a substrate, the first is by using a plate that carries the ink to the substrate. The second is by printing from a digital file of the image. Typically, the first is used in more commercial settings than the second. Lithographic inks are generally printed with an offset process, which is a form of commercial printing that is used in a vast number of major industries around the world including books, newspapers, and packaging. In lithographic printing, a plate is used. As seen in figure 1 below, offset printing gets its name from an additional cylinder, the blanket (offset) cylinder, which is used to help protect the plate from wear damage. Dirt or other particles that may be on the substrate can severely damage the printing plate. In commercial settings, using a blanket cylinder can lead to greater use out of the printing plate and longer use of each plate.

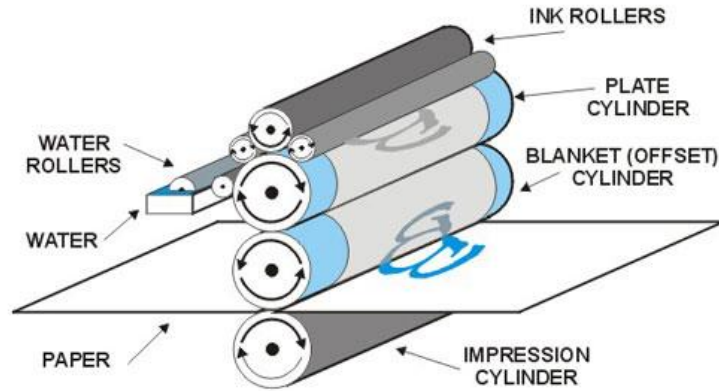


Figure 1. Offset Lithographic Printer⁵

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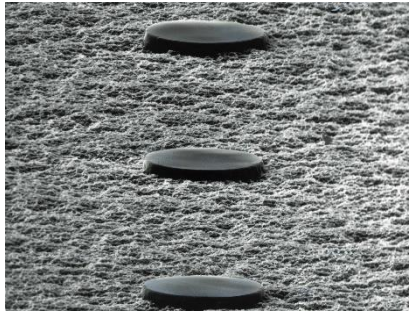


Figure 2. Lithographic Printing Plate⁶

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In Figure 1 , there is also a series of rollers before the plate cylinder.⁵ These rollers are used to transfer the ink to the plate. As previously mentioned, lithographic inks are oil-based inks, this is important for the printing process because the plate is designed with two different materials regions, a hydrophobic and hydrophilic material. This can be seen in Figure 2 where the circle is a hydrophobic material and the surrounding material has a hydrophilic property.⁵ This difference in ink receptivity is what controls the separation between image and non-image area. The image portion of the plate is ink receptive, whereas the non-image area is water receptive. Before the ink is dispensed on the plate, a fountain solution is dispensed, and this is attracted to the hydrophilic portion of the plate. This helps to keep the ink in only the desired image area. Thus, when the material is placed on a piece of paper or some other material that the image is being transferred to, only the desired image is left.^{7,8}

2.2. Current Ink Technology

In the case of black lithographic inks the pigment is usually made with carbon black, a petroleum refinement by-product. Carbon black is made from the incomplete combustion of petroleum, during the gas phase of the reaction.^{9,10} As seen in Figure 3., this process begins with oil, gas, air, and some additives that aid in the production.¹⁰ After the carbon black is separated out, it can be reformed or refined based on consumer needs.

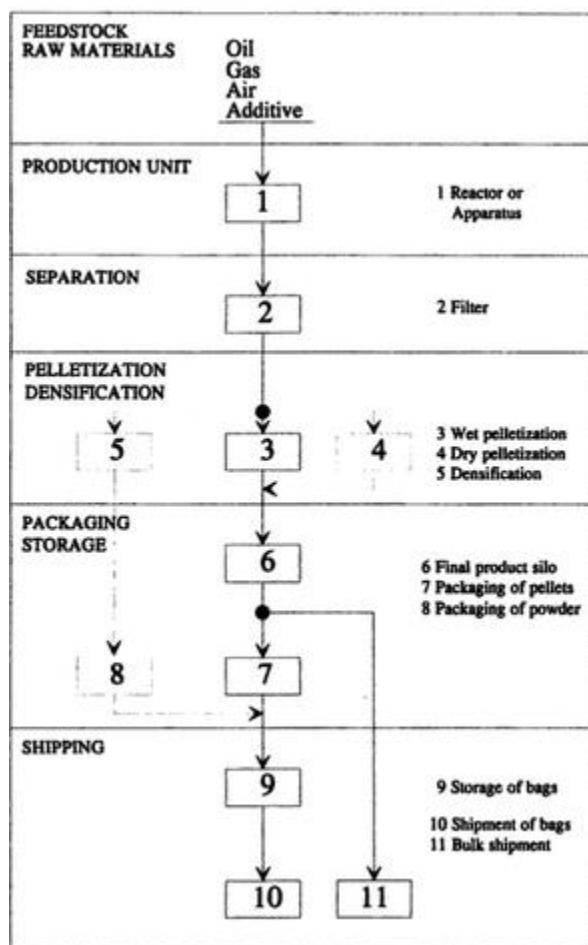


Figure 3. Carbon Black Production Process¹⁰

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Current black lithographic inks are made with a vehicle consisting of the material seen in Table 1. The components, other than the pigment, make up the ink vehicle. This vehicle is optimal for the printing properties necessary for lithographic prints, including the viscosity and dispersion effects it has on the pigment used. For this formula, any pigment may be used depending on the color required for the ink. For the purposes of this project, that is typically carbon black.

Table 1. Lithographic Ink Formulation¹¹

Raw Materials	% by weight
Pigment	23.00
Bodied Linseed Oil (20 Poise)	41.00
Phthalic Alkyd Resin	10.00
Phenolic Modified Penta Ester of Rosin	15.00
Polyethylene Wax (And/or Modified with Microcrystalline Wax)	3.00
Petroleum Distillate (C12-C16 Range, IBP=535F)	5.00
Cobalt and or Manganese Drier	3.00

2.3. Sustainability/Carbon Sequestration

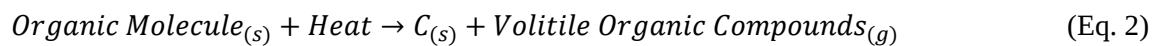
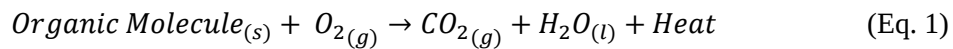
According to the United Nations World Commission on Environment and Development, sustainability is “development that meets current needs without compromising the ability of future generations to meet their needs.”¹² Due to the increased temperatures of the earth caused by large releases of carbon dioxide into the atmosphere, there is an increasing focus on making materials and processes more sustainable.¹³ There are several ways that the environment is currently being harmed by this increase in carbon dioxide emissions, the melting of polar ice caps, increases in sea levels, and an increase in the number of extreme weather events.^{13,14} A potential solution to the issue of global warming, is by reducing the amount of carbon dioxide emissions.

Carbon sequestration refers to the removal of carbon from the environment without additional carbon dioxide being released. Carbon positive refers to materials that introduce more carbon into the environment. Conversely, carbon negative materials are materials that reduce the amount of carbon; and therefore, the amount of carbon dioxide being released.

Carbon black is considered a carbon positive material because it is produced from petroleum. This introduces more carbon dioxide into the environment because the carbon is being removed from a sequestered place, buried underground, and reintroduced into the environment. In contrast, biochar is a carbon negative material because it takes organic waste materials from the environment that would normally be releasing carbon dioxide into a material that does not release carbon dioxide. The extent to which the carbon dioxide is prevented from being released is based on the individual biochar application. Through carbon sequestration, biochar applications counteract other worldwide carbon dioxide emissions.^{15,16}

2.4. Activated Carbon Forms – Biochar, Hydrochar, and Charcoal

Biochar is a form of carbon that is created from organic waste materials. Biochar is produced through a process called pyrolysis, a way of heating a material without oxygen present. Since there is no oxygen present, it prevents the substance from combusting and therefore creates a different product than burning the substance would make.¹⁷ The result is that there is much more carbon in the product, than there are other organic compounds, as seen in the combustion and pyrolysis equations, Equations 1 and 2 respectively.



Biochar is highly porous in nature. The porosity of biochar allows for adsorption of contaminant materials. For example, biochar porosity is the main reason behind the adsorption of heavy metals. The porosity of biochar leads to an increase in the total surface area of the biochar which is one property that enhances adsorption.¹⁸

Another important contributing aspect to the practical use of biochar, is the attached functional groups. During the pyrolysis process, certain functional groups may be left behind as a result of the heat. These functional groups aid in the efficiency of the material to adsorb contaminants.¹⁹ For example, biochars with a higher number of oxygen containing functional groups increases the adsorption of heavy metals including Pb^{2+} and Cu^{2+} onto the surface of the biochar. Other chemical and physical modifications can be made to the biochar after production to increase the sorption of other contaminants.²⁰ Amino modifications or acid/base treatments, magnetic modifications, methanol modifications, and combining the biochar with mineral sorbents can each adsorb cationic metals, iron containing compounds, organic contaminants, and phosphates or nitrates, respectively.

Lastly, biochar physical properties allow for a retention of water giving biochar an additional use in increasing plant growth.^{21,22} The large surface area and porosity of biochar allows for water to remain in the structure. This can be used as a water source for plants. Each of these properties, porosity and functionalization, of the biochar can be altered by changing the feedstock and pyrolysis conditions.²³

Activated carbon, which is a highly porous form of carbon, is very similar to biochar. However, a majority of activated carbon is produced from coal or other petroleum products, and biochar is made from any organic waste material. Activated carbon can be made with other feedstocks, however, including coconut husks.²⁴⁻²⁶

The largest difference between these two products is the ultimate use in each case. Biochar is typically used in cases where carbon sequestration is desired and activated carbon is generally produced with a focus on the application rather than the sequestration. This means that activated carbon may sequester carbon in some cases, such as when recycled materials are used as a feedstock.²⁴ However, activated carbon can also be made from virgin materials in some instances which can mean that sequestered carbon will be released back into the environment. The activation process for each is also very similar, including a physical or chemical activation process. Charcoal is also similar to biochar and activated carbon, but is

specifically made with woody biomass, whereas biochar and activated carbon can be made from other feedstocks.^{27,28}

Hydrochar is another form of activated carbon that has some similar applications to biochar but is made through a different process. Hydrochar is produced with lower heat and higher pressure in a process called hydrothermal carbonization (HTC). This process includes water to generate the high-pressure situation. Depending on the amount of water added in this process, the pressure inside the vessel changes.²⁹

2.5. Pyrolysis Process

Pyrolysis is a process where an organic material undergoes heating in an environment with little to no oxygen. In the absence of oxygen, there cannot be a combustion reaction. Combustion reactions, as seen in Equation 1, produce carbon dioxide and water as products. However, in pyrolysis, Equation 2, this technique produces carbon as a product. In other words, pyrolysis produces a solid, usable carbon product, whereas combustion produces CO₂.

Two main methods are used to heat the original feedstock, thermal and microwave radiation.³⁰ There are various temperatures at which the volatile organic compounds are released and at low enough temperatures, there will still be functional groups that remain. On the other hand, at certain high temperatures, all volatile organic compounds and thus functional groups will be removed from the feedstock. In addition, any inorganic materials that may be in the original feedstock will also be present after pyrolysis, typically as metal oxides.

In addition, pyrolysis of feedstock for the production of biochar can follow three main methods including but not limited to, slow pyrolysis, fast pyrolysis, and intermediate pyrolysis.³¹ Slow pyrolysis generally proceeds at lower temperatures than other forms with slow ramp rates and long residence times. Slow pyrolysis is mainly used when solid product is desired.³⁰ Fast pyrolysis uses short residence times, high temperatures, and faster ramp rates. Fast pyrolysis, for example, is used for bio-oil production. Intermediate pyrolysis proceeds at intermediate temperatures with about the same amount of liquid and solid produced.

2.6. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS/EDX)

Scanning electron microscopes use a beam of electrons that are sent toward a sample and produces an image as a result.³² The electrons are focused on the path toward the sample through magnet lenses.³³ When reaching the sample, these electrons excite the atoms in the sample and the result is electrons are emitted. Secondary electrons, back-scattered electrons, and x-rays are all emitted as a result. These electrons are scattered in various places depending on the depth of penetration. Secondary electrons are emitted from the surface of the sample, back-scattered electrons are emitted from a little deeper in the sample, and x-rays are emitted from the farthest in the sample.^{34,35} Each form of radiation is emitted at different angles, meaning multiple detectors are placed in various locations.³⁶

A primary beam of electrons is used to scan the sample. These electrons can either cause an ejection of an electron from the sample itself, or the electrons will simply stay in the sample. Conductive samples simply emit an electron which can then be detected and converted into an image. However, when insulating samples are analyzed, the electrons remain in the sample effectively charging it with more electrons. Samples used should be conductive to prevent this charging effect.

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a way of determining elements contained in a sample. This process can use the same set-up as the scanning electron microscope as the x-rays are also produced when an element is hit with an electron beam. The released x-rays are emitted at a 90° difference from the backscattered electrons used to generate the SEM image. This electron beam forces an electron to be removed from an inner shell, and an electron from a higher shell falls into the generated hole. When the electron falls into this hole, an x-ray is released that is relative to the gap between the two shells. Each element has specific energy gaps and thus specific x-ray energies as well., giving a specific spectrum. This spectra is quantitatively based on the quantity of x-rays produced, meaning it can give a relative amount of each element present.³⁵

2.7. Reflective Spectrodensimeter

Reflective spectrodensimeters are used to measure the optical density of a sample using a reflective geometry. Contribution of three subtractive colors cyan, magenta, and yellow can be obtained. Optical density is the measure ability of a material to block light from passing through. Lithographic inks must have a specific optical density in order for the image to appear the same to the human eye, regardless of the print.³⁷

For this study, the optical density of produced inks will be compared to the optical density of a standard ink.³⁸ Subtle changes in different color hues can affect the way black appears to the eye. Therefore, optical density measurements are important to this study, to ensure a true black color is matched. In the US, black pigments and inks currently used there is a larger presence of cyan than magenta or yellow. A higher optical density in cyan means a perceived blacker, or cooler, color. On the other hand, a higher optical density in magenta and yellow, relative to cyan gives a brown, or warmer-toned color. In order to match the ink covering power of current inks, the cyan, magenta, and yellow densities should also match. In addition, the overall visual optical density should also be the same in order to produce an ink that matches current inks.

2.8. Fourier-Transform Infrared Spectroscopy

Infrared Spectroscopy (IR) gives structural information about a sample being analyzed due to vibrational and rotational stretches in the molecule.^{39,40} The range that can be scanned in this method is from 4000-400cm⁻¹ due to the use of KBr beam splitter. This method can be useful because it is nondestructive. IR instruments send the wavelengths mentioned, toward the sample and the individual molecules absorb some of these wavelengths based on the bond. Different bonds have different stretches that correspond to a particular wavelength being absorbed.

Fourier-Transform Infrared Spectroscopy (FTIR) is a type of IR spectroscopy with the addition of an interferometer that can produce more accurate results.^{39,40} After light hits the sample, an interference pattern of light is produced from frequencies that are removed due to absorption by the sample. This interference pattern can in turn be analyzed using an interferometer. The interferometer measures the frequencies by converting them to spatial wavelength or wavenumbers. This interferometer contains two mirrors and a beam splitter which can be seen in Figure 4. The purpose of beam splitter is to recombine the beam of light

that is sent toward the sample meaning that all of the wavelengths of light are applied to the sample at the same time, decreasing the overall amount of time it takes to scan the sample. The beam splitter also determines what wavelengths can be scanned, as different materials absorb at different wavelengths.

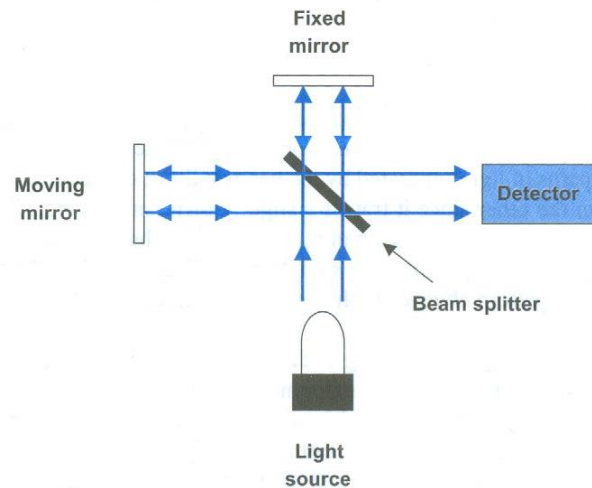


Figure 4. Interferometer Schematic³⁹

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CHAPTER 3 – REVIEW OF LITERATURE

3.1. Background Literature

3.1.1 Global Warming Issues

Anthropogenic global warming, caused by industrialization, poses many risks to the overall health of humans as well as a threat to wildlife. Theories have been developed on how the overall warming of the Earth can be slowed down or stopped altogether, including population restrictions and technological advances. However, another method that many scientists agree on is by reducing the amount of greenhouse gases that are released. These greenhouse gases are comprised of carbon dioxide, methane, nitrous oxide, and fluorinated gases.⁴¹ Among these, carbon dioxide is the most abundant.

Current black lithographic inks are made with carbon black, a product of the petroleum industry introducing more carbon emissions into the atmosphere.^{9,42} Biochar is a carbon negative alternative as it is a way to sequester carbon. Biochar adoption has the potential to offset CO₂ emissions, and is one current way to deal with carbon emission issues.^{15,43,44}

According to an estimate by Lee, J.W., et.al there is potential to offset carbon dioxide emissions by 38% through biomass conversion into sequestered biochar and biofuels. This estimate was based on the amount of biomass produced in the United States and an approximation of that biomass that is able to be converted into sequestered biochar and biofuels.

Some estimates indicate that petroleum stores are slowly decreasing, and may be at a point when petroleum products are no longer cost effective to manufacture.⁴⁵ Biochar is produced from organic waste which will theoretically never run out. Therefore, new pigment sources should be explored.

This project will mainly be focused on replacing carbon black with biochar. Currently, black ink is made from carbon black.⁴² One of the biggest issues with using carbon black is that it is a product of the petroleum industry.⁹ More specifically, it is a byproduct of petroleum combustion, whereas biochar is a more sustainable alternative.

3.1.2 Boxboard waste issues

Currently, there is an issue of not being able to infinitely recycle paper products such as cardboard.^{46,47} Instead, these products can only be recycled 5-7 times, before they are considered “non-recyclable” and are sent to a landfill. There is a limit to recyclability of paper products,

due to both fiber length issues and a hornification of fibers.^{48,49} As paper products are recycled more times, the fibers can become too short or no longer expand as necessary, which causes produced paper to fall apart and can cause contamination removal issues. These fibers are filtered out in the recycling process, during the filtration step.⁵⁰ Carbon dioxide is released into the atmosphere when the non-recyclable pulp is sent to landfill due to degradation..

Non-recyclable boxboard waste is a waste product and therefore includes inorganic fillers and inks.⁴⁹ TiO_2 and SiO_2 are both used as white pigments as well as brighteners in the recycling process due to their high refractive index. Other fillers and inks include kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5$) and Talc (Hydrous Magnesium Silicate – $3\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$).

3.1.3 Original Foundation of Biochar

Biochar has been used for centuries as a way to remediate soil. Ancient South American cultures used biochar, more commonly known in this context as Terra Preta.⁵¹ Terra Preta specifically describes the soil that is produced from biochar introduction.⁵² Biochar was mainly used because of poor soil quality in South America.⁵³ Terra Preta was a way to improve the quality of the soil and therefore increase crop production. Soil quality is improved because of the higher levels of organic matter, higher nutrient capacity, and a higher level of nutrients in the soil.⁵⁴ Biomass was charred underground. These underground conditions were such that biochar was produced in the soil itself.⁵⁵ In addition to South America, a similar amended soil containing the transformed biomass was also discovered in Germany.⁵⁴ The production of this altered carbon has not, until recently, become known as biochar.⁵⁶

3.2. Current Issues and Trends

3.2.1. Current Uses for Biochar

There has been a resurgence in biochar research, especially toward developing biochar for specific environmental applications.^{22,44,57} The main support for this comes from multi-beneficial properties of biochar, which can mitigate environmental crisis issues. Ancient biochar, known as Terra Preta, was used for soil remediation efforts and some current biochar uses were modelled after this. Specifically, there is experimentation on how biochar can be used for stabilizing the organic carbon in coastal wetland soil.⁵⁸ Deforestation processes are also inhibited by biochar introduction. When biochar is introduced to the soil in some rainforests, it

helps promote tree growth. This means that they can grow faster and better, leading to a decrease in the disparity in the number of trees being cut down and the number of trees growing.⁵⁹ There is also biochar from bamboo that is being used to help with desulfurization. Yang, E. et. al showed that biochar can be reused multiple times when recycled properly.⁶⁰ Biochar is also currently being investigated on its effectiveness on removing petroleum from contaminated soils.⁶¹ In addition, biochar has been shown to eliminate active ingredients in wastewater produced from pharmaceutical production.⁶²

3.2.2. Biochar Production

Biochar is produced through the pyrolysis of organic matter.⁶³ Pyrolysis is a process that heats biomass in low oxygen conditions giving it unique adsorption properties for environmental uses. There are different factors that can be altered during this pyrolysis process that can lead to different biochar properties.⁶⁴ Factors that can be altered include feedstock, pyrolysis parameters (temperature, residence time, ramp rate, etc.), and functionalization processes after pyrolysis.⁶⁵

3.2.3. Hydrochar and Current Uses

Hydrochar has similar uses as biochar, but is made with a different process.³¹ In hydrochar production, a liquid component along with the solid component is produced. Hydrochar may be more efficient and economically desirable because the feedstocks do not need to be pre-dried, thus eliminating a processing step.³¹ Process reductions also mean that other feedstocks can be used, including agricultural and municipal wastes.⁶⁶ Other feedstock that have been tested by other researchers include biomass feedstocks such as woody and lignocellulosic feedstocks and wastes from commercial palm oil production.^{67–69}

Recent research indicates that the hydrochar process can be used to produce bio-oils.^{70,71} To produce a bio-oil, the solid portion of the product is removed as biochar and the remaining liquid is treated in various ways to produce an oil. Other researchers are testing various chars produced from the HTC process to determine heating values.^{72,73} Many include varying the temperature and the biomass-to-water ratios.

3.2.4. Current Trends in Lithographic Inks

Lithography is a form of commercial printing that is used to produce printed books, newspapers, and packaging. All inks are composed of a pigment and a way to suspend that pigment and transfer it to a substrate. For black lithographic inks the pigment typically is carbon black.⁴²

3.2.5. Current Uses for Coal

Currently, coal is used in many different applications, but many of them include the combustion of coal for heat and electricity. In the United States, about 39% of all electricity produced was done so by the use of coal combustion.⁷⁴ This accounts for about 93% of the total coal consumed in the United States. The remaining percentage is used in industrial heat and power plants (7%), commercial (<1%), and residential and transportation (<1%).⁷⁵ This equates to a total of 4.11 trillion pounds of carbon dioxide. However, finding a use for this coal that is not associated with combustion, can reduce the carbon footprint of coal, without the destruction of the entire industry.

3.3. Conclusion

Biochar has mainly been used for soil and water remediation efforts. The similar hydrochar has also been used for these applications in addition to use for bio-oil production. Neither have been used in the production of pigments for any purposes including lithographic inks. In addition to printing inks, biochar may replace carbon black in other applications.

Adding sustainability to inks is a way of making a positive environmental impact. The largest impact can be made by removing the carbon black from the process and substituting the more sustainable biochar or hydrochar. Another way to decrease the emission of carbon dioxide is to use boxboard waste that is currently being landfilled as a feedstock for these. Another potential way to decrease carbon emissions is to use coal as a pigment as well, which can decrease the emissions from the combustion process that is currently being used.

Chapter 4 – PROBLEM STATEMENT

The main issue with current black lithographic inks is the sustainability issues with the current pigment carbon black. Replacing carbon black with an alternative and sustainable carbon source, biochar, in lithographic printing inks was researched. Biochar derived from innovative and renewable feedstocks, such as non-recyclable boxboard waste, was used. There was a particular focus placed on developing efficient methods to remove inorganic impurities in the feedstock. This is novel research in the area of developing sustainable lithographic pigments from biochar, a waste feedstock. This research will lead to more sustainable pigments and therefore more sustainable black lithographic inks.

Chapter 5 – METHODOLOGY

5.1. Materials

The feedstocks used were nonrecyclable boxboard waste, unused paper pulp, composted alpaca manure, and non-composted alpaca manure (Hemlock Hills Alpaca Farm, Hemlock, New York). The paper products were received from a local recycling plant. The chemicals used for pre-treatments included sodium hydroxide pellets (Macron Fine Chemicals), phosphoric acid (Aqua Solutions Inc.), sulfuric acid (EMD Millipore), hydrogen peroxide (Acros Organics), linoleic acid (Acros Chemicals), oleic acid, titanium dioxide (Dupont), and low-molecular weight chitosan (Sigma-Aldrich). Chemicals used for ink production included ethanol (Koptec), linseed oil (Eco-House) and stand oil/alkyd resin (Williamsburg Artist Oil Mediums).

5.2. Methods

5.2.1. Instrumentation

5.2.1.1. Scanning Electron Microscopy (SEM)/Energy Dispersive X-Ray Spectroscopy

A JEOL IT100 InTouchScope SEM/EDS was used. Samples were first dried in a (Fisher Scientific) drying oven at 65°C before being placed in the SEM/EDS. Samples were placed on aluminum stubs with carbon tape covering the top. The instrument was used in both high- and low-vacuum modes based on the conductivity of the sample.

5.2.1.2. Energy Dispersive X-Ray Fluorescence Spectrometer (EDXRF)

A Shimadzu EDXRF 8100 was used. The sample cup used was polypropylene with a 10mm collimator. The measurement type was Qual-Quant, sample form was bulk, compound form was metal, and it was scanning only for carbon, oxygen, silicon, calcium, and titanium. The voltage was kept constant at 5kV, current was 100μA, filter #2 was only used for calcium and titanium. The integration time was 100 seconds for silicon, calcium, and titanium, and 250 seconds for carbon and oxygen. The EDXRF sample was run under vacuum. Before being analyzed, the sample was pressed into a pellet with approximately 1.5 US tons of pressure.

5.2.1.3. Fourier Transform Infrared Spectroscopy (FTIR)

A Shimadzu FTIR was used. Both liquid and solid samples were analyzed without drying. Parameters included 45 integrations, a resolution of 4.0, and the range scanned was 400-4000 cm^{-1} .

5.2.1.4. Spectrodensimeter

An X-Rite Model 500 spectrodensimeter was used. Ink samples were first block printed and then placed in the scanning area. The spectrodensimeter was calibrated before every use, with blank white office paper.

5.2.2. Biochar Pyrolysis

Four biochar samples were used for ink production. Two were received from Cornell University, where the feedstock was anaerobically digested dairy manure and eastern pine wood chip. According to production parameters provided, these were pyrolyzed at 550°C with a residence time of 30 minutes.⁷⁶ After receiving these, they were pyrolyzed again to 1600°C at a rate of 15°C/minute with a residence time of one hour, resulting in two additional biochar samples to be used for ink production. Previous biochar samples produced were made from non-recyclable boxboard waste.

For pyrolyzed samples specific to this study, a high temperature furnace with inert gas (nitrogen) was used. The ramp rate was 10-15°C/min to 1600°C, with a residence time of 30-60 minutes. Finally, the furnace was allowed to cool at a natural rate, the samples were left overnight and removed the following day.

5.2.3. Feedstock Pre-Treatments

5.2.3.1. Refining in a Warring Laboratory Blender

Samples blended were added to a Warring Laboratory Blender with various amounts of water as indicated by individual treatments. Some samples were blended with tap water and others were blended with deionized water, again based on the individual treatment. Pressurized air was used to run the blender. Both high and low speeds were employed for every sample. The samples were refined in the blender around 10 minutes total, on average, not including stopping time. Samples were blended, until visually uniform throughout.

5.2.3.2. Calcium Removal Treatments

5.2.3.2.1. Phosphoric Acid Treatment

One gram feedstock was added to 200mL 1M phosphoric acid of feedstock, was added to a 250mL beaker with a stir bar. The sample was placed on a hot plate at 90°C with stirring for 1 hour. After 1 hour, the heat was turned off and the sample was left to continue stirring for an additional 12 hours. The sample was vacuum filtered with a Buchner funnel, rinsing with water until the filtrate was neutral. The sample was then removed from the funnel and left to dry overnight in a drying oven at 65°C.

5.2.3.3. Titanium Removal Treatments

5.2.3.3.1. Acid Digestion

0.63g non-recyclable boxboard waste and 14.9g of 0.01M sulfuric acid (pH 2.0) were added to a Parr high pressure acid digestion vessel. The reaction vessel was then placed in a ThermoScientific Thermolyne Oven which was heated to 150°C with a ramp rate of 7°C/minute and a residence time of 20 hours. The oven was allowed to cool naturally at which point the sample was removed and vacuum filtered. The solution pH was neutral and was therefore only rinsed three times with deionized water. The remaining boxboard was dried in a drying oven at 65°C.

5.2.3.3.2. Sulfuric Acid Treatment

A solution of 7.5M sulfuric acid was prepared. 100mL of the sulfuric acid solution was added to a 150mL beaker with a stir bar. 0.4g of Dupont Ti-Pure TiO₂ was added and the beaker was heated at 80°C with stirring for two hours. No change was observed, so the temperature was increased to 95°C for two additional hours. Again, no change was observed, so the temperature was increased one final time to 105°C for two additional hours before being set to 95°C overnight. After cooling, the sample was vacuum filtered, dried in a drying oven at 65°C, and re-weighed.

5.2.3.3.3. Base Digestion with 3% NaOH

0.62g of Dupont Ti-Pure TiO₂ was added to a 15mL Parr reactor with 17.3g of 3% NaOH. The reaction vessel was placed in a ThermoScientific Thermolyne Oven which was heated to 180°C with a ramp rate of 10°C/minute and a residence time of 48 hours. After removing the sample from the oven once cooled to room temperature, the sample was vacuum filtered and rinsed with water until the pH was neutral before being placed in a drying oven at 65°C. After completely dry the sample was reweighed, giving a 13.2% percent loss of the TiO₂.

5.2.3.3.4. Chitosan Treatment

The procedure used was based on TiO₂ flocculation tested by Divakaran, R., et. al. 0.1264g of chitosan was added to a 150mL beaker with 10mL of 0.1M HCl solution and stirred with a stirbar until mostly dissolved. The chitosan solution was then added to a 100mL volumetric flask and any remaining chitosan was rinsed into the flask with water before diluting to volume. 5.23mg of TiO₂ particles was added to a 1.5L beaker with either deionized water or tap water based on the experiment. This was stirred for several minutes with a stirbar before being sonicated for 20 minutes. 1.5mL of the previously prepared chitosan solution was added to the beaker. Additional 0.1M hydrochloric acid and 0.1M sodium carbonate solutions were prepared for pH adjustments, but pH strips indicated a neutral pH, so they were not used. The resulting solution was stirred at 60rpm for 30 minutes before being allowed to settle for an additional 30 minutes.

5.2.3.4. Silicon Removal Treatments

5.2.3.4.1. Soak Treatments

5.2.3.4.1.1. Deionized Water Soak

Non-recyclable boxboard waste was added to a beaker with deionized water to approximately 20% by weight. A stir bar was added, and the solution was allowed to stir for four days. The boxboard was then decanted off the top and the remaining contaminants stuck to the bottom of the beaker were removed separately. Each portion was vacuum filtered separately before being analyzed.

5.2.3.4.1.2. 3% NaOH Soak

Boxboard samples were added to a beaker with 3% NaOH in a 1:40 by weight ratio of boxboard to NaOH. The solution was left to sit for at least 16 hours. The solution was filtered in a Büchner funnel without filter paper. The sample was rinsed with water until the filtrate ran neutral in pH.

5.2.3.4.1.3. 3% NaOH Treatment

1.69g of Sigma Aldrich SiO₂ nanopowder, 10-20nm particle size (BET) was added to 100mL of 3% NaOH in a 150mL beaker. The solution was heated at 80°C with a watchglass on top of the beaker for at least 16 hours. At the end of the 16 hours, the sample was completely dissolved. This test was attempted again with the same amount of SiO₂ but was only heated for 3 hours and the SiO₂ was completely dissolved.

5.2.3.5. General/Multiple Contaminant Removal Treatments

5.2.3.5.1. Hydrogen Peroxide

The hydrogen peroxide treatment was performed directly after the phosphoric acid treatment. Once the sample had been removed from the drying oven it was placed in a 100mL round-bottom flask with aluminum foil around it. Approximately 30mL of Acros Organics hydrogen peroxide, ACS reagent, 30 wt% solution in water, non-stabilized, was added to the round-bottom flask and the sample was placed in a reflux set-up. The sample was allowed to reflux overnight. After reflux, the feedstock was vacuum-filtered and rinsed with water until neutral. The removed sample was a light green color and the filtrate was a clear orange/brown color with a pH of approximately four.

5.2.3.5.2. Flotation Treatment

5.2.3.5.1 Single Flotation Cell

One gram of boxboard waste was added to a 250mL two-neck round-bottom flask with 0.25g of oleic acid diluted to volume with 100mL of water and a stir bar was added. A septum was placed over one neck of the flask. A needle was put through the septum that was hooked to air with the needle being toward the bottom of the flask to produce the bubbles. A connector was added to the other neck of the flask that also connected to a second

two-neck round-bottom flask on a ring stand. One the second neck of the second round-bottom flask a tube was connected that led to a beaker to collect the bubbles. An image of this can be seen in Figure 5.

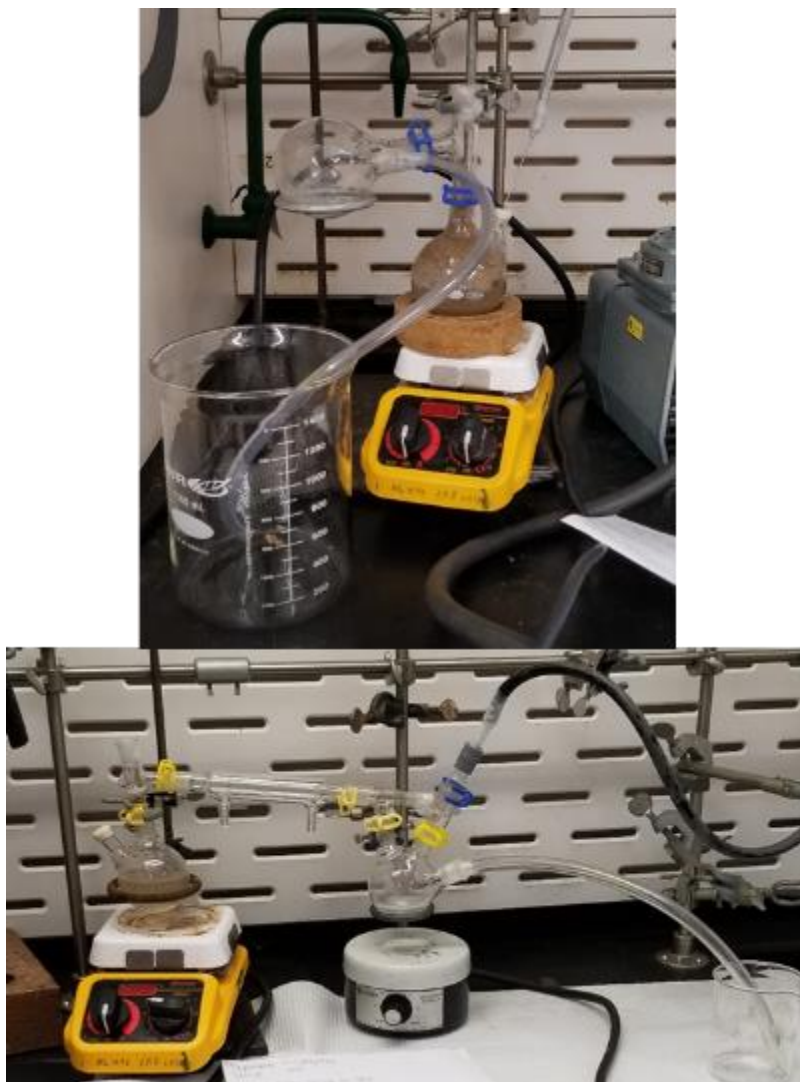


Figure 5. Flotation Cells

Cells pictured were developed and used, including a single flotation cell (top) and a double flotation cell (bottom).

5.2.3.5.2 Double Flotation Cell

The percentages used in this set-up were based on amounts used in the current paper recycling process as outlined in Gullichsen, J., et. al.⁴⁸ 0.5g of boxboard waste was added to a 50mL volumetric flask. Next 0.26g of oleic acid and 0.08g of glycerol were added. The solution was diluted to volume with 48.96g of 3.16×10^{-6} M NaOH. The solution was vortexed until small bubbles began to form. This solution was added to a 100mL two-neck round bottom flask for the final apparatus. In a second condition, 0.14g linoleic acid and 0.04g glycerol were added to a 25mL volumetric flask before diluting to volume with 24.65g of 3.16×10^{-6} M NaOH. This solution was vortexed until small bubbles began to form before being added to a 50mL three-neck round-bottom flask. *Apparatus set-up:* Flotation cell 1 was put on a ring stand over a stir plate. One neck was covered with a septum and a needle connected to air was placed through the septa toward the bottom of the liquid. A connector was added to the second neck of the first round-bottom which was then connected to a condensing tube. The other end of the condensing tube was connected to one of the necks on the second flotation cell. A second neck on the second round-bottom flask was connected to an additional air supply through a septum with a needle to produce bubbles in the second round-bottom. The third neck on the second round-bottom was connected to a tube which led to a beaker to collect bubbles. The second round-bottom flask also contained a stirbar and was over a stir plate. An image of this can be seen in Figure 5.

5.2.4. Hydrochar Production (HTC)

All hydrochar samples were produced using a 15mL Parr high pressure acid digestion vessel placed in a Thermo Scientific Thermolyne muffle furnace. Following the HTC reaction, the sample was removed from the oven and filtered using vacuum filtration. Some samples were rinsed only with water until the liquid ran clear and others were rinsed with acetone as well. Samples were analyzed using FTIR and EDS. Both solid and liquid samples were dried in a drying oven at 65°C before being analyzed by EDS. Hydrochar samples were produced at various temperatures, ramp rates, residence times, and pressures. The temperatures ranged from 180-280°C, ramp rates ranged from 5-20°C/minutes, residence times ranged from 0-6 hours, and pressures were estimated to be about 10-30 bar.

5.2.5. Biochar Vehicle Incorporation

The carbon black standard ink, made with Cabot BP2000, was made as the control ink. The optimized ink formula 17% pigment, 17% alkyd resin, and 66% linseed oil was developed with carbon black and was the starting point for the inks that followed to determine how well they matched.

5.2.6. Preliminary Block Printing

All biochar samples were ground to 1 μ m or less using a ball mill with various milling media, including ceramic, steel, glass, and copper. Ethanol was used to improve and speed up the milling process, with a 1:1:50 ratio of biochar: ethanol: milling media as per Peterson, S. et. al.⁷⁷ The samples were milled in 10-15 minute increments with time in between to allow for adequate cooling until the particle size was found to be less than 1 μ m by SEM.

Chapter 6 – RESULTS AND DISCUSSION

For biochar production, feedstock refers to the starting material before pyrolysis. This feedstock can have a large effect on the final biochar product including, functionalizations, porosity, and inorganic contaminations based on its own composition. Elemental carbon is produced when the reactants are only organic compounds. When inorganic compounds are present, the pyrolysis products tend to be non-volatile metal oxides. These inorganic compounds, while helpful in some remediation efforts,²⁰ can pose an issue with ink making in process milling or final ink color quality,^{78,79} especially mineral oxides used as fillers and inks found in paper waste materials. With the high temperatures used in pyrolysis, some inorganic filler compounds, such as kaolin, become stable inorganic anhydrous oxide or aluminosilicate compounds, and are more difficult to remove after pyrolysis.⁸⁰ A focus was placed on pretreating the feedstock (see Figure 6), prior to pyrolysis, to improve milling efficiency and pigment quality. Finally, lithographic inks were prepared using biochar pigments.

Several pre- and post-pyrolysis treatments were investigated as described in Section 6.3. All treatments are summarized in Figure 6. Treatment steps are color-coded based on effectiveness. Treatments color-coded in red were less effective while green coded processes were shown to be successful in removing targeted impurities. Of the treatments on the feedstock (pre-treatments), all were done using non-recyclable boxboard waste.

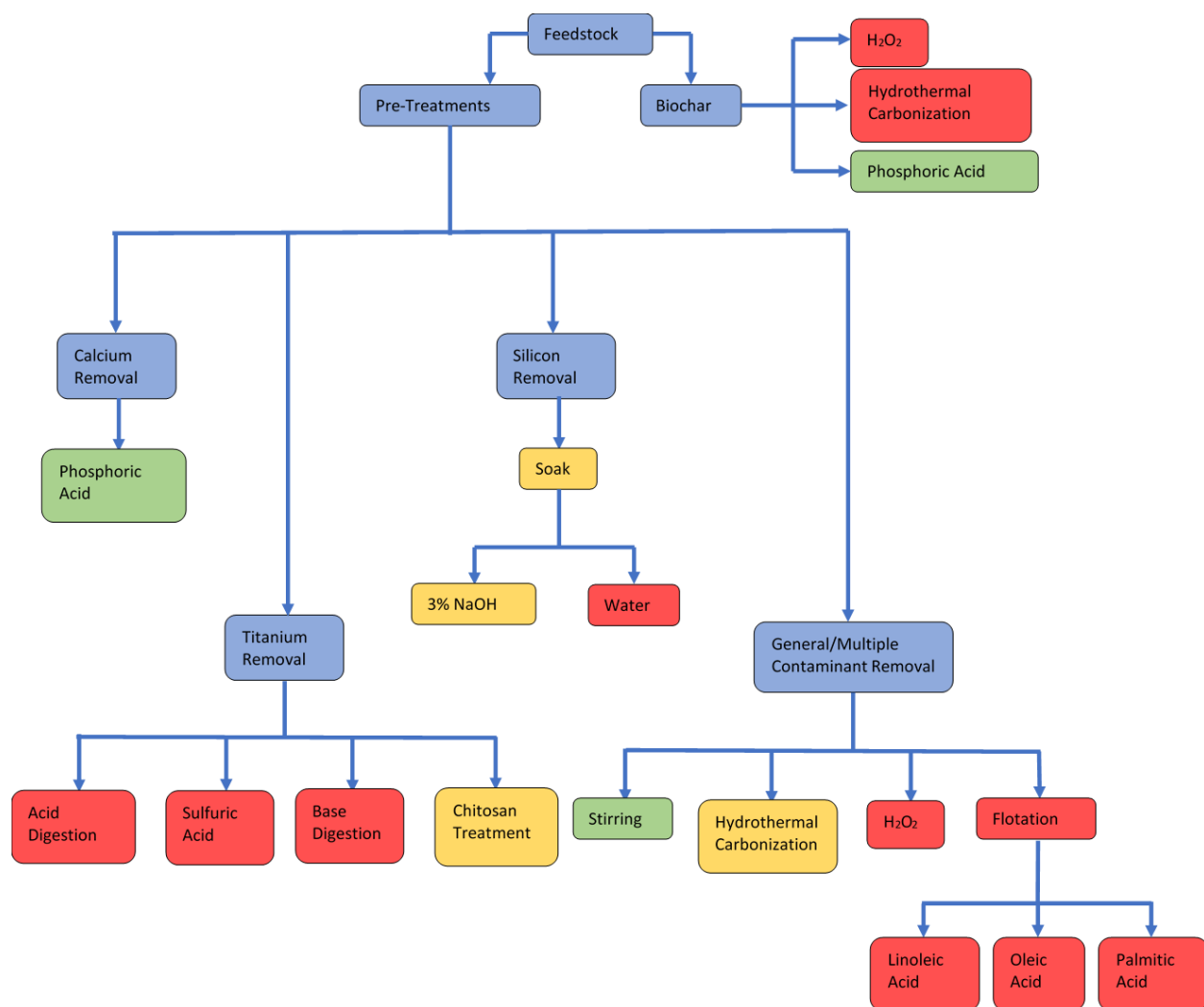


Figure 6. Boxboard Waste Pre-Treatment Tests

The red boxes below indicate pre-treatments that removed inorganic contaminants poorly, yellow boxes indicate results that plausibly remove inorganic contaminants, and the green boxes indicate results that accurately remove inorganic contaminants.

6.1 Raw Feedstock Sources and Composition

Feedstocks included alpaca manure (raw and composted), unused office paper pulp, and non-recyclable boxboard waste. The alpaca manure and unused office paper pulp were mainly used for hydrochar production, while the non-recyclable boxboard waste was mainly used for biochar production. As waste products, post-consumer paper feedstocks pose contamination issues of the biochar from inorganic compounds. Therefore, methods were developed to remove

these compounds before and after pyrolysis. Non-recyclable boxboard waste was chosen as the main feedstock to undergo treatment attempts to remove unwanted inorganic compounds (contaminants). Table 2 shows the original composition of each feedstock including the contaminants determined using energy dispersive x-ray spectroscopy (EDS) analysis. In Table 3, the original composition of the non-recyclable boxboard waste and unused office paper pulp were analyzed using an energy dispersive x-ray fluorescence analyzer (EDXRF). Both EDS and EDXRF results are consistent with known pigments amounts used in both office paper and boxboard.⁴⁹ Office paper is much whiter than brown boxboard, therefore, more CaCO_3 pigments should appear in the white office paper. Since the sample interrogation volumes/areas are vastly different with these two x-ray analysis techniques, some variation may be expected.⁸¹

Table 2. EDS Data for Original Feedstocks
Values given in percentage

	Unused Office Paper Pulp	Non-Recyclable Boxboard Waste
Carbon	56.85	93.16
MgO	-	0.14
Al₂O₃	0.51	0.66
SiO₂	-	1.53
Cl	0.36	-
SO₃	-	-
TiO₂	-	-
CaO	42.28	4.50

Table 3. EDXRF Data for Original Feedstocks
Values given in percentage

	Non-Recyclable Boxboard Waste
Carbon	93.057
Si	1.048
Ti	0.091
Ca	2.804

The most concerning of boxboard contaminants are the paperboard fillers including CaCO_3 , TiO_2 , and aluminosilicates ($\text{AlO}_2\text{-SiO}_2$), as they are the most abundantly present. This is also a potential issue when grinding the biochar down to a size suitable for pigment use ($<1\mu\text{m}$). It can be more difficult to mill biochar due to vast differences in material hardness. The optical properties of the TiO_2 and SiO_2 also decrease the covering power of the black pigment due to high optical refractivities.⁴⁹ Therefore, reducing these contaminants, would result in a blacker ink and shorter grinding times. There were two routes taken to remove these contaminants to improve the overall ink quality. The first was to remove the contaminants before pyrolysis, and the second was to remove them after pyrolysis.

6.2 Blending and Refining Treatments

Some of the samples were refined in a blender before undergoing contaminant removal treatments. To determine the effectiveness of the fiber refinement process, experimentation was performed with a phosphoric acid pre-treatment, to determine if future samples should be refined this way. Three boxboard samples were tested, one sample was refined without water, one sample was refined with water, and a control sample was also used without any refinement. Each sample underwent the same phosphoric acid pre-treatment (section 6.5). As indicated in Table 4, the sample that had been refined in the blender with water, showed the highest carbon content. The largest decrease in calcium oxide was observed in the sample refined with water. The smallest decrease in calcium oxide was noted in the control sample that had not been

refined. The phosphoric acid treatment is employed to remove calcium oxide from the feedstock and this data indicates the removal was most effective in the boxboard refined in a blender with water. Therefore, feedstocks used in all subsequent tests were first refined in a blender with water.

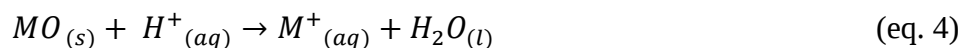
Table 4. EDS Results of Soaking/Stirring Boxboard in Water
Values given in percentage

	Carbon	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
Non-blended Boxboard	89.59 ±12.40	0.59 ±1.31	0.26 ±0.57	0.53 ±0.13	7.29 ±9.35	0.73 ±0.36	0	0.03 ±0.06	0.88 ±1.69	0.05 ±0.11	0
Boxboard Blended without Water	96.38 ±2.61	0	0.07 ±0.15	0.48 ±0.08	2.83 ±2.75	0	0.13 ±0.09	0	0.02 ±0.04	0.10 ±0.09	0
Boxboard Blended with Water	96.51 ±4.13	0	1.18 ±2.35	0.59 ±0.39	1.53 ±1.32	0	0.13 ±0.10	0	0	0	0.08 ±0.17

6.3. Calcium Removing Treatments

6.3.1. Phosphoric Acid Treatment

Phosphoric acid can be used as a method of removing metal oxides through an acid/base reaction. Metal oxides are basic and therefore when they are treated with acids, the result will be a soluble salt in water, as depicted in Equation 4 for a monobasic metal oxide.



As Table 5 shows, the phosphoric acid pre-treatment increased the overall carbon percent, and almost completely removes the calcium from the sample. Therefore, this treatment was determined to be effective for removing calcium and magnesium mineral contaminants.

Table 5. EDS Data from the Phosphoric Acid Treatment

Values given in percentage

	Carbon	MgO	Al₂O₃	SiO₂	SO₃	TiO₂	CaO
Before Treatment	93.16	0.14	0.66	1.53	-	-	4.50
Phosphoric Acid Treatment	96.38	0.07	0.48	-	0.13	0.10	0.04

6.4. Titanium Removal Treatments

6.4.1. Acid Digestion

An acid digestion, also using sulfuric acid, was employed to dissolve mineral oxides through an acid-base reaction process. The main difference between this treatment and the previous sulfuric acid treatment, is that this treatment was done in a Parr high pressure acid digestion vessel, rather than a beaker. Based on the EDS data seen in Table 6, however, the acid digestion treatment decreased the overall carbon percent, meaning it was not as effective as a single treatment at removing contaminants as other methods. Percent carbon decrease could have also been due to some disintegration of the boxboard itself during the process. This was evidenced by the liquid that was removed from the acid digester, as seen in Figure 7. The filtrate liquid was slightly brown in color, which is most likely due to an increase in soluble functionalized carbon. The removed filtrate had a neutral pH, indicating a reaction occurred. However, this was most likely with the paper fiber in the boxboard, as confirmed with the EDS results in Table 6. This treatment should be tested in future experiments in tandem with a base treatment to determine effectiveness of contaminant removal.

Table 6. EDS Results After Acid Digestion

Values given in percentage

	Carbon	MgO	Al₂O₃	SiO₂	SO₃	TiO₂	CaO
Before Treatment	93.16	0.14	0.66	1.53	-	-	4.50
After Acid Digestion	90.40	-	0.99	1.47	0.72	0.34	6.07



Figure 7. Removed Liquid from Acid Digestion

6.4.2. Sulfuric Acid Treatment

The sulfuric acid treatment was tested with pure TiO_2 particles, based on previous work done by Short, F.J. et. al. Of the 0.4031g of TiO_2 added to the sulfuric acid solution, 0.3738g remained after filtering. This means there was only a 7.26% loss or 0.0293g of the TiO_2 dissolved in 100mL of 7.5M sulfuric acid. The sulfuric acid treatment was also heated to near boiling for approximately an hour. This treatment was therefore, not optimal for continued experimentation using the non-recyclable boxboard waste. Concentrated sulfuric acid, heated near boiling, would degrade any boxboard fibers remaining in the sample. This evidence suggests that dissolution of TiO_2 is possible but would not produce a desired outcome for the dissolution of TiO_2 for biochar derived from non-recyclable boxboard waste.

6.4.3. Base Digestion with 3% NaOH

Further experimentation was done on TiO_2 , based on additional precedent found in Man, L.F., et. al using a Parr reactor with 3% NaOH. This base digestion treatment of the TiO_2 dissolved approximately 13% TiO_2 , with 0.0821g of the original 0.622g of TiO_2 added to the reaction vessel. However, this treatment method also required longer digestion times to dissolve the TiO_2 . With heating in the reaction vessel for 48 hours, this treatment is also not optimal for use with non-recyclable boxboard waste, due to concerns of boxboard degradation. At higher

temperatures and pressures, the boxboard would likely also dissolve in the 3% NaOH. This was further evidenced by the amount of boxboard degradation with the simple 3% NaOH treatment in a beaker outside the Parr reactor, which had milder conditions associated. Therefore, this treatment method was not tested with the non-recyclable boxboard waste.

6.4.4. Chitosan Treatment

Divakaran, R. et. al reported on a method for pH dependent TiO_2 flocculation experiments and this was investigated as a potential method for removing the TiO_2 .⁸² Their results showed, that tap water was more effective at flocculating TiO_2 than distilled water, using a pH of around 7.5. Th chitosan treatment used a solution of chitosan and HCl. The same process was attempted for this project. The mechanism driving this reaction forward, according to Divakaran, R. et. al, is that natural organic matter found in tap water, adsorbs on the surfaces of the TiO_2 molecules, generating more negative surface charges. At this point, the chitosan binds the molecules together by bridging between them, creating larger sized particles, flocs at close to neutral pH.

Figure 8 shows suspended TiO_2 particles in deionized water before and after the chitosan treatment. The images show that there was no change in the particles after the treatment and was not used in further experimentation. A second iteration of this experimentation was performed, with tap water used instead of deionized water to increase the ionic strength, and create flocs as described by Divakaran, et. al. Figure 8 shows that this change was enough to flocculate the TiO_2 particles, allowing for removal from the water. However, in this case, the flocculation was most likely from metals found in the tap water complexing to the TiO_2 . Flocculation indicated this may be a suitable procedure for TiO_2 removal from non-recyclable boxboard waste as well.

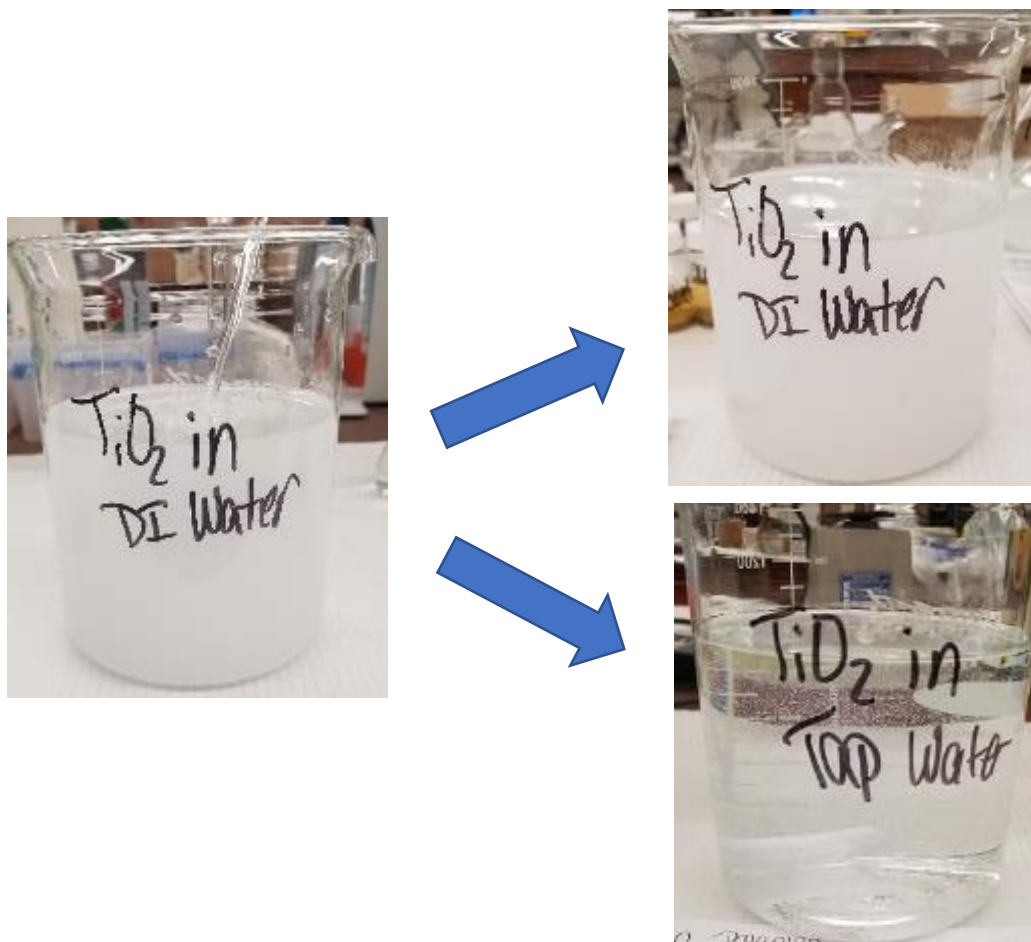


Figure 8. TiO_2 Flocculation Experiment in Deionized Water

Figure shows beaker after first adding TiO_2 (left), after treatment initially in deionized water (top right), and after treatment with the change to tap water (bottom right).

The tap water - chitosan treatment was attempted with the non-recyclable boxboard waste. However, as Figure 9 demonstrates, this was not an effective treatment. No flocculation was seen with the non-recyclable boxboard waste after stirring for 30 minutes and resting for 30 minutes. This could be potentially because of the low amount of TiO_2 in a paper sample. Another explanation could be that the TiO_2 in the non-recyclable boxboard waste, had not been released from inside the fibers, due to hornification of the fibers. If the TiO_2 remained stuck in the fibers, it would not be close enough to the chitosan to flocculate.

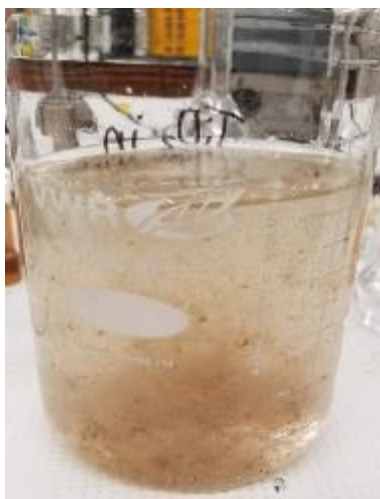


Figure 9. TiO₂ Flocculation Experiment with Non-Recyclable Boxboard Waste

Figure shows beaker with non-recyclable boxboard waste in tap water after chitosan treatment, showing no flocculation of TiO₂

6.5. Silicon Removal Treatments

6.5.1. Soak Treatments

Soak treatments are generally employed in the recycling process to loosen the fibers and release some of the contaminants caught inside the fibers.⁸³ Throughout the recycling process, there is wetting (soaking) and drying of the fibers. As this process proceeds forward, these fibers are less likely to stretch and open again, this process is known as hornification.⁴⁸ Fiber hornification is one obstacle to the fibers being indefinitely recycled. As the fibers become stiff, it becomes more difficult to remove the inks and fillers. The more inks and fillers that remain in the fibers proportionally decreases pulp quality, rendering the final product useless.

The soaking processes were modelled after those used in the recycling process, for the same end goal, to remove inks and fillers. However, unlike the soaking process used for paper recycling⁴⁸, final pulp quality is no longer important. Lastly, some fibers can be removed as unusable if they are too stiff.

6.5.2. Deionized Water Soak

Soaking in deionized water was initially used as a control for 3% NaOH soaking. However, upon stirring over several days, small particles were found settling on the beaker bottom, as demonstrated in Figure 10. After the component separation, the remaining boxboard was decanted off the top. Table 7 shows the carbon percent increased after stirring, and the removed portion contained a high amount of mineral calcium.



Figure 10. Settled Boxboard Waste After Stirring Treatment

Boxboard waste after stirring 3 days. White circle indicates area where settling occurred

Table 7. EDS Results of Soaking/Stirring Boxboard in Water
Values given in percentage

	Carbon	MgO	Al ₂ O ₃	SiO ₂	SO ₃	TiO ₂	CaO
Boxboard Waste	93.16	0.14	0.66	1.53	-	-	4.50
After Stirring in Water	97.30	-	0.33	1.02	0.07	-	1.28
Removed Contaminants from Stirring	85.51	1.05	0.90	3.80	0.14	0.20	8.22

6.5.3. 3% NaOH Treatment

Healey, E. demonstrated a method for removing unwanted contaminants from paper products during the recycling process.⁸³ Their method was employed to soften the fibers, releasing trapped contaminants, making the contaminants easier to remove. Their method includes soaking fibers in 3% NaOH for at least 16 hours. In addition, a 3%NaOH treatment can be useful in removing silicon dioxide from the non-recyclable boxboard as well, through the production of silicates as noted in Equation 3.



An initial test and rerun of results described by Healey,E. was performed with approximately 1.7% w/v SiO₂ was dissolved in 3% NaOH. Figure 11. illustrates the transition from suspended silicon dioxide to dissolved silicon dioxide in the 3% NaOH after stirring at 90°C for 16 hours. 3% NaOH dissolves suspended silicon dioxide particles, according to Equation 3. Additional experimentation determined that the reaction time could be reduced to two hours. The dissolution of the SiO₂ gives evidence that this method may be useful in removing SiO₂ from non-recyclable boxboard waste. Therefore, further experimentation was performed using boxboard.

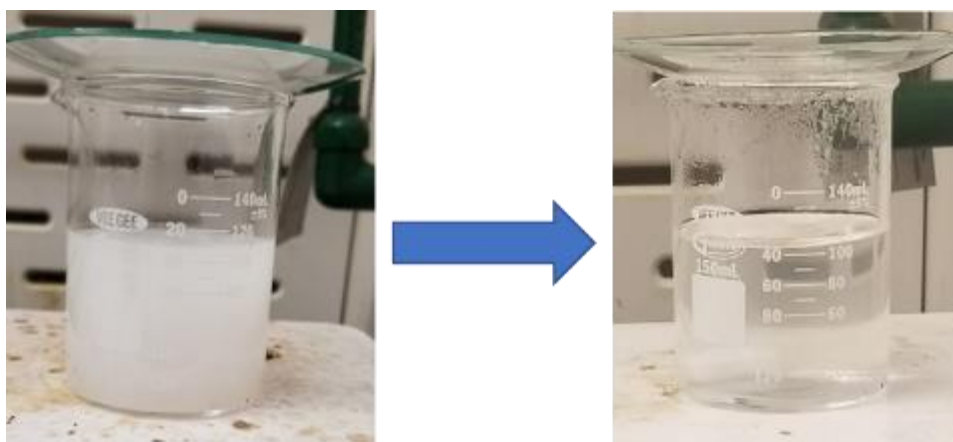


Figure 11. 3% NaOH Treatment Experiment

Silicon dioxide particles suspended in 3% NaOH (left) and dissolved after stirring at 90°C for 16 hours (right).

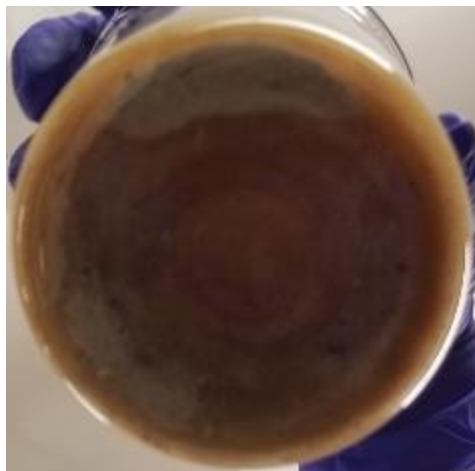


Figure 12. Boxboard Waste After Stirring for 12 Hours in 3% NaOH

When the boxboard was treated in the same method, no removal of SiO_2 was observed. This was confirmed with EDS data, as seen in Table 8. This could be due to other reactions occurring between the NaOH and other contaminants or the boxboard itself. Other issues include heating during the entire 16 hours, which may also disintegrate some of the boxboard and therefore could be the cause of the reduction in the carbon percent. EDS results are relative to the amount of each compound in the sample, so with a decrease in carbon, there would also be an increase in the other compounds. Future experimentation should be performed on boxboard in 3% NaOH to determine degradation effects and an optimal heating time.

Another possible explanation is that the SiO_2 was not pure in the case of the boxboard, as it was with the preliminary test. Instead there may be a size difference, or it could be an aluminosilicate. Evidence is seen for aluminosilicates, as there was also no decrease in the Al_2O_3 after treatment. Either difference would result in a different outcome than the pure nanoparticle SiO_2 used in the preliminary test. Future experimentation should be done on aluminosilicates to determine similar results.

Table 8. EDS Results for 3% NaOH Treatments

Values given in percentage

	Carbon	MgO	Al₂O₃	SiO₂	SO₃	TiO₂	CaO
Before SiO ₂ Treatment	93.16	0.14	0.66	1.53	-	-	4.50
After Soaking Treatment (No Heating)	93.71	0.05	0.82	1.56	0.07	0.04	3.72
After SiO ₂ Treatment (Heating with 3% NaOH)	89.69	0.26	0.71	2.68	0.11	0.12	6.32

6.6. General/Multiple Contaminant Removal Treatments

6.6.1. Hydrogen Peroxide Treatment

Hydrogen peroxide treatments can be used as a method of oxygenating the biochar.²⁰ Hydrogen peroxide is a strong oxidizer, meaning there is potential to add oxygen to the compounds and therefore, increase the solubility of the contaminants.. All hydrogen peroxide treatments were attempted in succession after a phosphoric acid treatment. Based on the EDS data seen in Table 9, the degradation of the boxboard was more favorable, leading to a decrease in overall carbon from the sample. It is possible that the inorganic compounds contained in the sample are too stable to be affected by the hydrogen peroxide. Another option that should be explored is altering the order of treatments. The hydrogen peroxide treatment may be used as a preparation step for the phosphoric acid treatment. The contaminants may be oxygenated in the hydrogen peroxide step but are not being solubilized. By treating the feedstock with hydrogen peroxide before treating with phosphoric acid, the phosphoric acid treatment can be a way to remove the contaminants after the oxygenation step. A last option is that the hydrogen peroxide treatment is breaking down some of the boxboard fibers and thus releasing more of the inorganic contaminants. Once these contaminants are released, it may be easier to remove them. Again, this could be optimized by introducing an acid treatment directly after this step. The hydrogen peroxide treatment can be used as a method of releasing more contaminants stuck in the boxboard fibers, that can then be removed through a secondary treatment step.

Table 9. EDS Data from Hydrogen Peroxide Treatment

Values given in percentage

Note: This treatment was performed after a phosphoric acid treatment, explaining why there is no calcium.

	Carbon	MgO	Al₂O₃	SiO₂	TiO₂	Fe₂O₃	CaO
Before Any Treatment	93.16	0.14	0.66	1.53	-	-	4.50
After Phosphoric Acid Treatment	94.99	-	0.54	3.33	0.06	-	0.13
After Hydrogen Peroxide Treatment	85.93	0.91	3.31	8.74	0.66	0.13	-

6.6.2. Flotation Treatment

Flotation treatments are a method of removing inks and fillers currently used in the recycling process.⁴⁸ This method employs soaps and surfactants to remove hydrophobic contaminants through agitation using bubbles. These unwanted particles attach themselves to the outside of the bubbles. Since all contaminant particles are not hydrophobic, surfactants are added to increase removal effectiveness. After attaching, the bubbles are skimmed off the top of the boxboard mixture, removing the contaminants and leaving the boxboard fibers. The probability of ink attachment on bubbles is based on many factors, including two phase interfacial tensions and contact angle.⁸⁴

A similar process was used in this study, to remove unwanted inorganic contaminants. Lab-scale flotation cells developed were based on industrial-scale flotation set-ups. The flotation cells were designed to remove bubbles from the system as they were generated. The three organic compounds used as soaps were linoleic, oleic, and palmitic acids, based on compounds currently used in the paper recycling industry.^{48,85} Each fatty acid was used separately, except in the case of the double flotation, when a different compound was used in each cell. However, this flotation treatment, did not alter the boxboard mixture, due to issues in the process. More specifically, effective bubbles were not produced in the flotation cells, meaning that no contaminants could attach to the bubbles and be removed. Of the bubbles produced, they popped before there was a change for the bubbles to be removed from the system. In the case of the

double flotation, no bubbles progressed to the second cell, meaning no boxboard or contaminants could progress either. Therefore, any contaminants that may have attached to these bubbles would not have been removed from the overall solution. Due to issues separating the solution from the feedstock, the contaminants could not effectively be removed this way. Since there was no contaminant removal, no further analysis was done. Future experimentation should include more testing to optimize surfactant bubble production.

Of the pre-treatments attempted on the original feedstock, the most effective as single treatments included the phosphoric acid treatment and the stirring treatment. Both treatments removed unwanted inorganic contaminants without degrading the boxboard. The least effective treatments, such as the hydrogen peroxide and acid digestion pre-treatments, should be attempted again as multi-step processes. For example, these two pre-treatments should be performed on the same sample in tandem to determine their overall effectiveness. In both cases, there was a degradation of the boxboard that was interfering with the contaminant reaction. Both treatments that removed inorganic contaminants poorly should be optimized to determine if they can be implemented into a future recycling process with non-recyclable boxboard waste.

Another major issue noted in some of the poorly effective pre-treatments was hornification. Some of the data indicates that the contaminants are still trapped in the fibers, which shows some evidence that the waste fibers cannot be recycled again. Based on the evidence shown above, the hornification of the boxboard fibers may be too severe at this point to be recycled even by these methods for use in biochar. To determine the effect of fiber hornification, the same processes should be performed on virgin pulp and the results should be compared. One potential solution for this problem may be to destroy some fibers in the process to still be able to recycle some. In degrading some of the fibers and removing them, there may be a higher likelihood of removing inorganic contaminants. In this case, there would need to be an analysis included of the percentage of boxboard still being recycling and which option is truly more sustainable.

6.7. Hydrothermal Carbonization Treatment (Hydrochar Production)

Hydrochar analysis as a suitable substitute was performed due to the desirable physical properties, such as grindability and there is no need to pre-dry the feedstock.⁶⁹ The main feedstocks used to produce the hydrochar included alpaca manure (raw and composted), office paper pulp (unused), and non-recyclable boxboard waste. After the hydrochar was created, both the solid samples as well as the removed liquid were analyzed using EDS and FTIR. Table 10 shows all hydrochar sample parameters. Parameters were chosen based on standard hydrothermal carbonization parameters as outlined by Kambo, H.S., et.al, Feng, S.H., et. al, and Parr reactor operating instructions.^{29,31,86} The base parameters were modelled after Kambo, H.S., et. al, the water added during the HTC process was based on Figure 4 in section 2.4 from Feng, S.H., et. al, and the residence temperature was based on the upper limit of the specific Parr reactor used. A survey of various parameters was conducted.

Table 10. Hydrochar Processing Parameters

Sample Number	Feedstock	Feedstock to Water Ratio (g:g)	% of Autoclave Full	Heating Rate	Residence Temperature	Residence Time
1	Composted Alpaca Manure	1:8	-	7°C/minute	220C	0 Hours
2	Unused Paper Pulp	1:16	-	7°C/minute	275C	3.5 hours
3	Unused Paper Pulp	1:16	-	7°C/minute	275C	3 hours
4	Boxboard Waste	1:10	-	7°C/minute	275C	3 hours
5	Unused Paper Pulp	1:32	50%	7°C/minute	275C	3 hours
6	Boxboard Waste	1:10	-	5°C/minute	275C	3 hours
7	Unused Paper Pulp	1:32	-	7°C/minute	275C	3 hours
8	380C Currency Biochar	1:16	-	7°C/minute	275C	3 hours
9	Unused Paper Pulp	1:32	-	7°C/minute	275C	6 hours
10	Unused Paper Pulp	1:55	70%	7°C/minute	275C	3 hours
11	Boxboard Waste	1:8	80-90%	7°C/minute	275C	3 hours
12	Unaltered Alpaca Manure	N/A	80%	7°C/minute	275C	3 hours
13	Unaltered Alpaca Manure	5:1	-	7°C/minute	275C	3 hours
14	Unused Paper Pulp	1:42	90%	7°C/minute	220C	3 hours
15	Unused Paper Pulp	1:56	90%	7°C/minute	225C	3 hours
16	Unaltered Alpaca Manure	1:2	80%	7°C/minute	275C	3 hours
17	Unused Paper Pulp	1:54	80-90%	20°C/minute	265-285C	1 hour
18	Unused Paper Pulp	1:65	-	7C/minute	275C	3 hours

The most impactful factor noted, based on EDS data as seen in Figure 13., was both the percentage of the reactor that was full and the feedstock to water ratio. Figure 13 highlights the change in feedstock to water ratio and indicates that as the water was increased relative to the feedstock, there was a larger carbon output of the solid hydrochar material. This could be due to more efficient hydrolysis and conversion when less feedstock was present. Figures 14 and 15, show two hydrochar samples. These images show that the hydrochar was a browner color than

the biochar. Since, a black ink is ultimately desired, this testing was suspended. Future contributions should continue looking at hydrochar as a sustainable alternative to current pigments. Even though these pigments may be inferior in color when compared to current pigments, if branded as sustainable or created as a byproduct for bio-oil production, they may still be suitable.

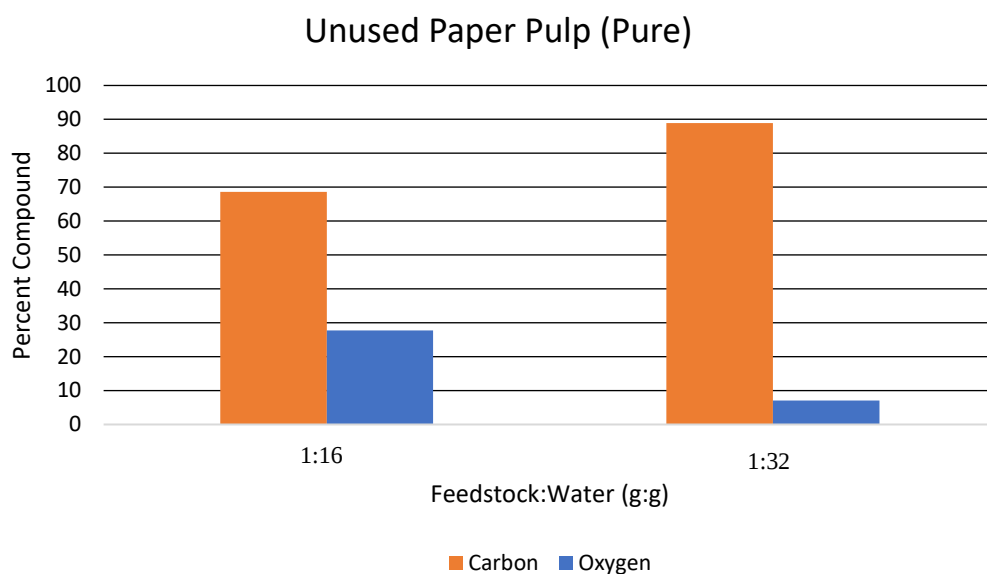


Figure 13. EDS Data of Carbon and Oxygen for Samples with Unused Paper Pulp as the Feedstock



Figure 14. Hydrochar 4 Solid



Figure 15. Hydrochar 5 Solid on Filter Paper

6.8. Biochar Data

6.8.1 Pyrolysis Attempts

Pyrolysis was attempted with and without a nitrogen atmosphere. The resulting samples contained minimal amounts of carbon. Figure 16 and 17 show the result from an attempted pyrolysis without an inert gas used. Figure 16 shows the color of the sample, it appears white rather than the brown/black of typical biochar. EDS results suggest the white product was ash rather than carbon (Figure 17).



Figure 16. Pyrolysis Sample 1

Sample was pyrolyzed in a Lindberg/Blue oven without Nitrogen, unused paper pulp heated to 1100C for an hour

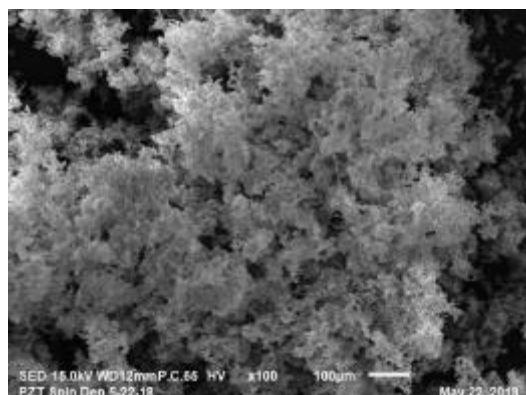


Figure 17. SEM Image and EDS Results of Pyrolysis Sample 1

This method can additionally be used for determining the mineral content in samples after treatment, as most of the carbon was removed. In the case seen above, however, there was still some carbon remaining in the sample. In future testing, EDS data based on samples heated in a muffle furnace, can be used to determine relative amounts of inorganic content left.

6.8.2 Biochar Production with Temperature

Biochar received from Cornell University, showed increases in carbon percent upon reprocessing at the higher temperature as confirmed with EDS results in Table 11 and 12. This indicates that as processing temperatures increase, the product will become darker, due to an increase in Carbon (see section 6.9.2 for more information). There is also a noted decrease in MgO in Tables 11 and 12.

Table 11. EDS Data from Cornell Anaerobically Digested Dairy Manure Biochar

EDS data for original and reprocessed biochar with standard deviations shown.

Anaerobically Digested Manure	Carbon content	CaO Content	SiO ₂ Content	MgO Content	Other
As Received	87.29%±3.82%	8.53%±2.88%	1.45%±0.33%	1.18%±0.27%	1.55%
After Heating to 1600C	91.89%±3.61%	5.36%±2.66%	1.93%±0.60%	0.25%±0.14%	0.57%

Table 12. EDS Data from Cornell Pine Wood Chip Biochar

EDS data for original and reprocessed biochar with standard deviations shown.

White Pine Wood Chips	Carbon Content	SiO ₂ Content	CaO Content	Other
As Received	96.54%±2.11%	1.27%±1.10%	0%	2.19%
After heating at 1600C	98.58%±1.23%	1.16%±0.96%	0.11%±0.07%	0.15%

6.9 Lithographic Ink Formulation using Biochar

6.9.1 Ink Standard Data

Ink standards were produced with the same method as all other inks produced.



Figure 18. Carbon Black Standard Print

6.9.2 Produced Ink Data

Prints of inks made with various biochar pigments can be seen in Figure 19. The images of the prints show that the inks produced are comparable to one another. When the prints with biochar pigments seen in Figure 18 are compared to the carbon black print in Figure 19, the ink appears similar.

Anaerobically Digested
Manure (550°C)



Pine Wood Chip (550°C)



Coal



Pine Wood Chip (1600°C)



Figure 19. Prints Produced with Novel Pigments

Prints produced from anaerobically digested manure biochar pigment, pyrolyzed at 550°C (top left), pine wood chip biochar (550°C) pigment (top right), pine wood chip biochar (1600°C) pigment (bottom right), and coal pigment (bottom left)

The produced inks were all made with 17% pigment. As seen in Table 13, the visual density of the biochar ink, derived from Cornell anaerobically digested manure pyrolyzed at 550°C, was overall slightly lower than the standard ink produced. Additionally, the ink was a warm color consistent with a higher visual density in the magenta and yellow compared to cyan. The remaining two biochar inks with pigments produced from Eastern Pine Wood Chip. The

resulting ink still had a warmer color than the carbon black standard. The ink produced using a sample of the Eastern Pine Wood Chip biochar from Cornell that had been re-pyrolyzed at 1600°C had a slightly higher visual density, especially in the cyan meaning it was cooler and therefore it matched the standard better. The ink produced with a coal pigment was cooler than some of the biochar inks as it had a visual density of 1.36 in cyan compared to the 1.33 in magenta and 1.28 in the yellow. This was the largest disparity in the colored visual densities of inks produced from materials other than carbon black.

Table 13. Visual Density of Produced Inks

Visual Density	Carbon Black Standard	550°C Anaerobically Digested Manure Biochar	550 °C Eastern Pine Wood Chip Biochar	1600 °C Eastern Pine Wood Chip Biochar	Coal
Visual	1.92	1.32	1.36	1.45	1.35
Cyan	1.93	1.31	1.36	1.45	1.36
Magenta	1.91	1.33	1.37	1.44	1.33
Yellow	1.84	1.33	1.35	1.39	1.28

Chapter 7 – CONCLUSION

7.1. Conclusion of Results

Techniques were developed to remove inorganic contaminants including mineral calcium, titanium and silicon from biochar feedstock. Additionally, a survey of hydrochar parameters for pigment production was presented. Lastly, preliminary prints were produced with biochar pigments, showing similar visual density results as the standard carbon black inks. This study has developed methods for use in pigment production from waste materials by a conversion to biochar/hydrochar. More broadly, this research can be applied to other biochar application where inorganic contaminants are unwanted.

7.2. Novel Contributions

This research demonstrates a pathway for contaminant removal from non-recyclable boxboard waste. Three contaminants were attempted to be removed, mineral calcium, titanium, and silicon oxides. The phosphoric acid treatment was an effective method of removing the calcium containing contaminants. While not as repeatable, a stirring treatment was effective at removing some mineral contaminants including titanium, calcium, silicon, and aluminum containing particles. Other methods were developed and modified for future removal techniques including the chitosan and 3% NaOH treatments for removal of titanium and silicon respectively.

Lastly, novel contributions were made as a new black pigment was developed for lithographic inks. This pigment also shows potential for other ink types and other applications for black pigments. The optical density and carbon percentage results show that the black biochar pigments developed is comparable to the current carbon black pigment.

7.3. Recyclability of Non-recyclable Boxboard Waste

One of the major goals of this study was to develop a method for recycling a product that is being landfilled because of its recyclability limit. As previously mentioned, boxboard can only be recycled 5-7 times before the fibers can no longer produce an optimal paper product. This study was aimed at finding an additional use for this waste material to increase the number of times this material can be recycled. However, many issues were encountered, the greatest being the hornification of the fibers. Removal of the inorganic contaminants was made the most difficult by this fiber hornification. This was seen most in the treatments intended to remove the

TiO₂. Before additional work is done with the non-recyclable boxboard waste, more calculations on potential sustainability improvements should be performed, such as a Life Cycle Assessment (LCA). If there is a high probability for improvements in terms of environmental sustainability using non-recyclable boxboard waste as an ink pigment rather than other disposal methods, then experimentation should continue on contaminant removal. However, if the calculation results show no improvements in the environmental sustainability of recycling the non-recyclable boxboard waste, then further experimentation with inorganic contaminant removal should not be pursued further.

7.4. Future Work

7.4.1. Life Cycle Assessment (LCA)

A Life Cycle Assessments (LCA) is a calculation method used to help determine environmental costs of a product or process by analyzing its entire life cycle. LCA's can be used to help guide decision making, especially for new product development. An LCA of biochar or hydrochar produced from non-recyclable boxboard waste and carbon black should all be performed. All three LCA's should be compared to one another to help determine the true environmental sustainability of a replacement of carbon black. More specifically, an LCA would help answer the question of whether or not a switch to a more "sustainable" biochar or hydrochar pigment would actually reduce environmental impacts. The first step of performing an LCA is to define the goal and scope which helps create an objective assessment. Parameters for an LCA of biochar as a black pigment replacement should be as follows for a future study.

Goal and scope: The findings of this study would be to inform a scientist whether recycling non-recyclable boxboard waste into a biochar/hydrochar ink pigment is more environmentally sustainable than the use of carbon black in ink pigments. This study would not be intended for a public audience.

Function: To produce a black ink pigment.

Functional Unit: One metric ton of pigment produced.

Reference Flows Necessary: *Carbon black:* Amount of petroleum needed to produce 1 metric ton of carbon black, amount of carbon black transported at one time, method of transportation, average distance of transportation for use as a pigment, any additional processing necessary to produce a pigment (milling). *Non-recyclable boxboard waste:* Potential methods of

transportation, potential required distances of transportation, processing technique (HTC vs. pyrolysis), milling.

System Boundaries: *Biochar and hydrochar:* Previous impacts of waste materials used in production should not be included. Only from transportation of material to end of life as a waste material. *Carbon black:* From extraction of materials to the end of life as a waste material.

Assumptions: Each product (carbon black, hydrochar, biochar) is only being used for ink pigments. The waste materials used for hydrochar and biochar production are only used as waste materials.

Impact Assessments: Global Warming Potential, Global Warming Human Health

Sensitivity Analyses: Use various distances of transportation for materials, use different potential methods off transportation used (boxboard), use a survey of different amounts of boxboard waste being transported at one time, include a sample calculation with petroleum as an additional output of carbon black production.

7.4.2. Hydrochar Continuation

The hydrochar production in this project, as previously mentioned, does not seem suitable for use as a black pigment. This assessment is solely based on the assumption that inks cannot be made that don't meet the current specifications. The goal of this project was to produce a black lithographic ink that has the same qualities of current inks, but if a brown pigment is acceptable, hydrochar is a sustainable option.

Hydrochar is a more sustainable pigment than biochar because unlike biochar, there is evidence that this product has more useful properties, such as grindability and no need to pre-dry the feedstock.⁶⁹ In addition, hydrochar production can produce up to three end products including the solid hydrochar.⁸⁷ A higher value product that is also produced during the HTC process is bio-oil. The solid product gets used in a similar way that biochar does, meaning it may also be of use in ink pigment production. If the hydrochar solid product was used as an ink pigment, a system similar to the current carbon black production would be developed. Currently, carbon black is a byproduct of petroleum refinement, but there are many uses that have been found for carbon black. Similarly, hydrochar production could generate both a liquid oil product and a solid product that can have other uses, such as pigments or other carbon black replacements. The only true sacrifice would with the color. Hydrochar cannot produce as dark

and cool colors, so anything made with a solid hydrochar wouldn't appear as black to the observer.

Another issue with the hydrochar production in this study was the level to which it was studied. Only a survey of parameters was tested rather than focusing on particular parameters. Future work should be done on individual feedstocks and altering each parameter systematically to determine the best method for producing an ink pigment. Individual parameter effects on hydrochar produced should be investigated in a future study. Such parameters include the effect of temperature, feedstock, residence time, and ramp rate. Based on the assumption previously discussed that a pigment does not have to be as black as the current pigments used, new pigment parameters should be determined. A method should then be optimized from these parameters.

7.4.3. Titanium Dioxide Removal

Removing TiO₂ from non-recyclable boxboard waste may be too energy intensive, because of the extensive processes that must be employed, to be more sustainable than a virgin material. The measures that would have to be taken to fully remove the TiO₂ would be extreme. There is potential to turn TiO₂ from a waste material into a new recycled product. There is some precedent in the literature for creating new TiO₂ products with similar methods used in this study, such as HTC.^{88,89} HTC methods to remove TiO₂ were attempted in this study, with only slight success. However, the methods used in this study, did not directly follow those found in the HTC literature for TiO₂ conversion, which is an area of continued study.

Additional literature shows other potential methods for the removal of TiO₂ similar to the flocculation method used in this study.⁹⁰⁻⁹² However, unless a usable TiO₂ product can be made from the non-recyclable boxboard waste and two recycled materials are produced, the TiO₂ should not be a focus to remove.

7.4.4 Flotation Optimization

Lab scale flotation methods should continue to be developed. There are many areas of improvement in the recycling industry, but the flotation method used is still an optimized method of contaminant removal. To move innovation in paper recycling forward therefore, an optimized lab scale process should be developed. A flotation method for contamination removal would also be useful if this work were to be continued.

7.4.5. Pre-Treatments vs. Post-Treatments

Previous members of the Williams group developed methods for the removal of calcium containing contaminants through the use of a phosphoric acid treatment. This work employed the same treatment method before pyrolysis with the feedstock. Both methods are effective at removing the calcium containing contaminants found in various feedstocks and biochar, especially the non-recyclable boxboard waste studied in this work. No tests were done however, on the relative effectiveness of this treatment. Future tests should be performed to determine if treatment with phosphoric acid is more effective before or after pyrolysis, or if they are equally effective.

7.4.6. TAPPI Standards

As previously mentioned, the pigments produced in this study are not optimized to the current TAPPI ink standards. Additional experimentation should be performed on optimizing the biochar pigments produced to match current TAPPI standards. Such ink performance tests should include the grind test (ASTM #D1316), the tinting strength test (ASTM #D2066), the transparency (opacity) test (ISO #2846-1), the viscosity test (ASTM #D2196-10), the water pick-up test (ASTM #D4942), the tack test (ASTM #D4361), and the drying test (ASTM #D5909). It should also be determined if additional processing is necessary to match these standards. If additional processing is necessary, it should also be determined whether the TAPPI standards need to continue being followed for black ink pigments or not.

As discussed in section 7.3.2., a determination should be made if a standard black color is relevant to consumers or not. A potential way to determine this may be through focus groups.

7.4.7. Other Materials

Other sustainable feedstocks should be further investigated as well. Non-recyclable boxboard waste was chosen because of the potential sustainable nature and previous group work. However, there are other materials that are more sustainable in nature than carbon black. Such materials include, manure products including raw, composted, and anaerobically digested which were all investigated to some extent in this study. Each new material comes with its own set of inorganic contaminants, so it may be easier to remove different contaminants than the ones found in waste paper products. The TiO_2 found in paper products was the largest barrier

to overcome in this project, but TiO_2 would not be found in all feedstocks. So, another way to produce a more sustainable black pigment may be to use different feedstocks.

7.4.8. Other Applications

There may be more potential for using biochar produced with non-recyclable boxboard waste for other applications. Carbon black is used in other applications, other than as a pigment, where color is not as much of an issue. One example is the use of carbon black in tires. In cases where the color of the carbon black replacement is not as important, biochar made from non-recyclable boxboard waste may be a suitable replacement. Depending on the ultimate application, there can be various amounts of cleaning of the feedstock or biochar. Applications that should be investigated in the future include, use in tires, use in structural materials, and soil and/or water remediation efforts.

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